Chemical vapor deposition of magnetic iron-cobalt alloy thin films: Use of ammonia to stabilize growth from carbonyl precursors

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In previous work, it was demonstrated that Fe₅−Coₓ(1−ₓ) alloy thin films with near ideal magnetic properties can be grown by chemical vapor deposition (CVD) from the precursors Fe(CO)₅ and Co₅(CO)₉; previous attempts to grow such films by CVD, using these or other precursors, had not been able to afford high saturation magnetization. However, it was found that the morphology and composition were extremely sensitive to small variations in the deposition temperature and the precursor partial pressures. In a second work, it was showed that the CVD of pure iron films from Fe(CO)₅ is subject to a self-poisoning effect in which the growth surface accumulates carbon, which causes the growth rate to decline progressively to zero. Then it was shown that the poisoning effect can be eliminated by adding a coflow of NH₃ during CVD, which does not introduce measurable quantities of nitrogen into the film. In the current work, the authors return to the compositional instabilities in Fe₅−Coₓ(1−ₓ) alloy growth and show that, as seen for pure Fe growth, these instabilities can be as attributed to a surface poisoning effect involving dissociative chemisorption of carbon monoxide. It was found that a coflow of ammonia, which inhibits CO adsorption, enables the growth of Fe₅−Coₓ(1−ₓ) films over a wide temperature window with highly reproducible morphology and stoichiometry. Alloys that were grown under the NH₃ coflow with suitable compositions (x ~ 0.6) achieve near ideal values of the saturation magnetization. Published by the AVS. https://doi.org/10.1116/1.5045671

I. INTRODUCTION

Iron-cobalt alloys are excellent soft ferromagnetic materials that are widely used in data storage applications such as writer heads for hard disc drives and magnetic tunnel junctions in spin-transfer torque magnetic random-access memories. Although the Fe₅−Coₓ(1−ₓ) alloys in such devices are currently sputter deposited, there is considerable interest in developing low temperature chemical vapor deposition (CVD) processes to deposit films of this material, so as to extend scalability to future technology nodes.

We recently described such a CVD process, in which the precursors Fe(CO)₅ and Co₅(CO)₉ afford Fe₅−Coₓ(1−ₓ) alloys with saturation magnetization near to the theoretical maximum of 2.45 T, relatively low coercivity, and good conformal coverage of trenches with 4:1 aspect ratio. We also reviewed previous efforts to achieve the CVD of Fe₅−Coₓ(1−ₓ) films from these and other precursors; those studies achieved saturation magnetizations only 10–42% of the theoretical maximum and did not report the coercivity or the conformal coverage. In that previous work, however, we found that the film composition and microstructure were unusually sensitive to the ratio of CVD precursor fluxes and to the substrate temperature. When the precursor flux ratio was varied from run to run in order to achieve the target stoichiometry (x = 0.5–0.7), the composition changed nonlinearly and often was accompanied by a significant change in the surface morphology. In addition, the temperature window to grow a high quality film was extremely narrow: around the optimum of 230 °C, a variation of only a few degrees would shift the film stoichiometry from Fe-rich to Co-rich relative to the desired stoichiometry. Furthermore, at higher growth temperatures, the Fe content was typically the greatest at the beginning of the deposit and decreased significantly as growth proceeded, i.e., the Fe/Co ratio varied with depth in the sample. These problems were overcome by strictly controlling the deposition temperature and precursor pressures to within very narrow ranges. However, the narrow process window meant that this solution was challenging to implement; moreover, the fundamental cause of the strong compositional and morphological variations remained unknown.

In separate work, we recently showed that Fe CVD from the Fe(CO)₅ precursor is strongly influenced by a surface poisoning effect in which CO groups dissociate on the Fe surface and form surface species that block active sites for Fe growth. An important (but not the only) pathway is the known reaction of adsorbed CO molecules to form surface C and release CO₂. Even though our previous work showed that the amount of surface C carbon formed was small, it is well known that even submonolayer coverages of carbon can poison a surface. The poisoning effect is enhanced at the elevated substrate temperature and also when the flux of CO to the surface is increased. We then discovered that this poisoning effect can be completely eliminated by coflowing NH₃ along with the Fe(CO)₅ precursor during growth; furthermore, the resulting Fe film does not contain measurable amounts of nitrogen. We proposed a mechanism in which adsorbed NH₃ displaces CO from the growth surface such that CO chemisorption is strongly inhibited, and adsorbed NH₃ eventually leaves the surface either intact or via disproportionation to N₂ and H₂.

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In the current work, we show that our previous observations of strong compositional and morphological variations in $\text{Fe}_x\text{Co}_{1-x}$ CVD are due to the same CO-derived poisoning effect observed in the growth of pure Fe films. We first describe the dependence of the $\text{Fe}_x\text{Co}_{1-x}$ alloy composition on the substrate temperature and the flux ratio of the Fe and Co carbonyl precursors and explain these dependencies in terms of surface poisoning of Fe sites. We then demonstrate that a coflow of NH$_3$ eliminates the unusual behavior such that the temperature window for $\text{Fe}_x\text{Co}_{1-x}$ growth is greatly enlarged, the film stoichiometry is stable and depends linearly on the precursor flux ratio, and the morphology is reproducible. The net effect of added ammonia is to make the CVD of $\text{Fe}_x\text{Co}_{1-x}$ thin films from Fe(CO)$_5$ and Co$_2$(CO)$_8$ a reliable and easily controlled process.

II. EXPERIMENT

$\text{Fe}_x\text{Co}_{1-x}$ films were grown in a turbo-pumped high vacuum chamber$^3$ with a base pressure of 10$^{-7}$ Torr. The substrate was air-exposed Ru (5 nm)/SiO$_2$ (300 nm)/Si, radiatively heated with a proportional-integral-derivative controlled heating box. The Fe(CO)$_5$ precursor reservoir was cooled to 0 °C in an ice-water bath, and the flux was regulated by a needle valve. The Co$_2$(CO)$_8$ precursor reservoir was held in a water bath at 23.0 ± 0.5 °C with no needle valve in the delivery line; this source gave a constant precursor partial pressure of 0.050 ± 0.003 mTorr for all experiments. In selected experiments, NH$_3$ gas was delivered as a coflow. NH$_3$ was distilled from sodium before use to remove traces of water.

The precursor fluxes were delivered to the chamber through separate stainless steel tubes pointing toward the cold chamber wall. Molecular flow scattering then created an isotropic flux in the chamber, i.e., the flux impinging on the substrate surface was proportional to the partial pressure of each precursor, which was measured in the absence of film growth (with the substrate unheated).

Compositional analyses were performed by means of Auger electron spectroscopy. Film microstructure and thicknesses were measured by SEM on fracture cross sections. Films intended for magnetic measurements were capped in situ with a layer of CVD grown HfB$_2$ to prevent oxidation upon air exposure.$^8$

Magnetic hysteresis loops were measured on a vibrating sample magnetometer (VSM). Both the easy and hard axes hysteresis loops were measured with the magnetic field oriented in the plane of the film. The magnetic moment was then normalized to the total volume of $\text{Fe}_x\text{Co}_{1-x}$, calculated from the sample area and film thickness measured by cross-section SEM. The total uncertainty in the magnetic moment from contributions of area, thickness, and VSM measurements is estimated to be ±10%.

III. RESULTS AND DISCUSSION

Our recent study of the self-poisoning effect during Fe CVD from Fe(CO)$_5$ provides crucial background for the present work,$^4$ hence, we summarize its principal results here. The central finding is that CO groups, which are released by the precursor during growth, react with the Fe surface to cause an irreversible decrease in the surface reactivity, associated with the buildup of carbon.$^9$ We reported that (i) the average Fe deposition rate decreases from 120 to 5 nm/min as the substrate temperature is increased from 200 to 300 °C; (ii) at a constant temperature of 300 °C, the growth rate decreases monotonically over time and after 10 min becomes zero (a self-limiting thickness); (iii) addition of CO to the process gas stream accelerates the poisoning effect; (iv) the progressive decrease in the growth rate is most likely caused by dissociative chemisorption of CO to form surface carbide species, which reduce the reactivity of (poison) the surface; the possibility that adsorbed CO molecules reduce the growth rate via surface site blocking or associative desorption of the precursor can be ruled out because such reversible reactions do not explain the observed irreversible reduction in the surface reactivity; (v) under conditions that lead to surface poisoning, the morphology no longer exhibits crystallographic facets, presumably owing to suppression of adatom diffusion; and (vi) addition of ammonia inhibits the surface poisoning effect by preventing the dissociative chemisorption of CO. For a fully detailed discussion of the mechanisms and relevant literature, we refer the interested reader to Ref. 4.

A. Co film growth

In sharp contrast to the CVD of Fe from Fe(CO)$_5$, we find that the deposition of Co from Co$_2$(CO)$_8$ is not significantly affected by surface poisoning. Whereas the Fe growth rate from Fe(CO)$_5$ decreases as either the temperature or growth time increases [observations (i) and (ii) above], Co growth from Co$_2$(CO)$_8$ onto a Ru seed layer exhibits classic CVD behavior for metals.$^9,10$ At a precursor partial pressure of 0.050 ± 0.003 mTorr and growth times of 10 min, relatively little deposition occurs at substrate temperatures below 90 °C because the reaction rate is too low. At a temperature of 90 °C, the growth rate is 2.5 nm/min, and between 100 and 300 °C, the rate is larger 6.5 ± 0.5 nm/min, and constant because under our conditions, the growth rate is flux limited [Fig. 1(a)]. Throughout this temperature range, the film microstructure is dense and smooth; the small variation in film thickness is consistent with the uncertainty in the Co$_2$(CO)$_8$ precursor partial pressure. Confirmation that the growth is flux limited under our conditions (and not limited by a poisoning effect, at least for growth times of 15 min or less) comes from the finding that, at a constant growth temperature of 300 °C, the Co film thickness increases more or less linearly with time [Fig. 1(b)], although there may be some slowing due to poisoning at times longer than 15 min.

The experiments of Fig. 1 indicate that Co growth in the absence of Fe is largely unaffected by surface poisoning for deposition times less than 15 min, but they do not distinguish between two alternatives: no dissociative chemisorption of CO occurs during growth, or dissociative chemisorption of CO does occur but the resulting carbon
exerts little or no poisoning effect. The dissociative chemisorption of CO on a Co surface has a higher activation barrier than on a Fe surface but occurs at temperatures above 100 °C. The evidence suggests, therefore, that some dissociation does take place, but the resulting adsorbed carbon does not greatly affect the rate of Co growth. We confirmed this conclusion by showing that Co can nucleate and grow quickly on a heavily carbon-poisoned Fe surface. We first deposited an Fe film at 300 °C for 10 min. As found previously, Fe growth ceased under these conditions and was unable to restart. Nevertheless, on this fully poisoned Fe surface, Co nucleated with zero incubation time at 300 °C and attained a thickness of 70 nm in 10 min (Fig. 2); this growth rate is the same as that observed when depositing Co directly onto the Ru seed layer at this temperature [Fig. 1(a)].

B. Fe$_x$Co$_{(1-x)}$ alloy film growth

The kinetic behavior we reported previously for the CVD of Fe$_x$Co$_{(1-x)}$ from Fe(CO)$_5$ and Co$_2$(CO)$_8$ is approximately a combination of the behaviors for pure Fe growth affected with surface poisoning (our previous observations) and for pure Co growth (the above experiments). The hypothesis that the carbon formed by CO chemisorption suppresses deposition of Fe but not Co explains our previous results that, under many growth conditions, the Fe$_x$Co$_{(1-x)}$ films are richer in Fe near the substrate interface (i.e., at the beginning of the deposition) but richer in Co near the upper surface (i.e., late in the deposition). Furthermore, the hypothesis that Fe growth shuts down more quickly as the rate of carbon formation increases explains why—for the same fluxes of Fe(CO)$_5$ and Co$_2$(CO)$_8$—films grown at lower temperatures (210 °C) were richer in Fe than films grown at higher temperatures (235 °C) at which the dissociative chemisorption of CO is faster.

In our earlier study, we showed that dense, smooth, and high-purity Fe$_x$Co$_{(1-x)}$ thin films could be grown by CVD from Fe(CO)$_5$ and Co$_2$(CO)$_8$, but only under very limited conditions: at relatively high fluxes and at temperatures within a few degrees of 230 °C. We now believe that, under these conditions, dissociative chemisorption of CO does occur but is relatively slow relative to the rate at which cobalt is deposited; the cobalt covers the small amount of surface carbon generated and renucleates the growth of additional alloy such that surface poisoning is avoided by a narrow kinetic margin.

1. Fe$_x$Co$_{(1-x)}$ growth as a function of temperature and pressure

We have carried out some additional experiments in order to further document how the dissociative chemisorption of CO affects the growth of Fe$_x$Co$_{(1-x)}$ thin films. In our previous study, we did not measure film growth rate as a function of temperature. We have now done so at a constant precursor partial pressure ratio of 2:1 [0.100 ± 0.003 mTorr of Fe(CO)$_5$ and 0.050 ± 0.003 mTorr of Co$_2$(CO)$_8$]; these conditions correspond to the “low flux” conditions in our previous work. For a constant growth time of 10 min, the total film thickness decreases from 200 nm at 175 °C to ~70 nm at 250 or 300 °C (Fig. 3). Although the former film is columnar, and therefore of lower density, the void space between the columns in the images is less than 70 vol.%; even if we correct for this
difference in density, the total deposition rate of material is smaller at higher temperature. This finding is inconsistent with reaction rate theory—in which the growth rate should increase with increasing temperature—but is entirely consistent with a surface poisoning effect that becomes more pronounced at higher temperatures owing to the faster CO chemisorption rate.

Our earlier study only briefly described how the morphology of the Fe$_x$Co$_{(1-x)}$ thin films changes with temperature: at 210 °C they were columnar, whereas at 235 °C they were dense and relatively smooth. We can now confirm this dependence over a wider temperature range: under low flux conditions, the Fe$_x$Co$_{(1-x)}$ films are columnar at both 175 and 200 °C but are smooth and dense at both 250 and 300 °C (Fig. 4). This trend is qualitatively similar to that observed for pure Fe growth, except that pure Fe does not become smooth and dense until 300 °C (some 75 °C hotter than the ca. 225 °C crossover point seen for the alloy films). We previously interpreted that the smooth morphology resulted from poisoning, which suppressed the growth of facets. For alloy growth, it is possible that smoothing occurs at a lower temperature due to the faster poisoning of Fe surface sites by the additional CO that is released from the Fe$_2$(CO)$_{11}$ precursor.

Auger sputter depth profiles (Fig. 3) further demonstrate the effect of Fe site poisoning on the film composition. At 175 °C, the Fe/Co ratio has a constant value of 3:1 at all depths in the film, indicating the absence of progressive poisoning. The oxygen in the film is primarily due to the diffusion of oxygen molecules through the intercolumn voids upon air exposure. This interpretation was confirmed by an experiment in which a Fe/Co film, grown under identical conditions, was capped in situ with HfB$_2$, which is a highly conformal diffusion barrier; in that sample, the measured oxygen content was only 1–2 at. %. The carbon content is relatively small in the interiors of the films (ca. 5 at. %) but is significantly larger at the upper (growth) surface, up to 30 at. %. The amount exceeds the submonolayer coverages of carbon that often are sufficient to poison many kinds of catalytically active surfaces.

At 200 °C, the vertically anisotropic nature of the deposit suggests that this film is the result of an intermediate state
between unpoisoned and fully poisoned growth. At 250 °C, the Fe/Co ratio shows a sharp decrease from 3:1 (Fe-rich) at the beginning of the growth to 1:3 (Fe depleted) at the end. We propose that this change is due to the poisoning effect, which slows the Fe growth rate but not the Co growth rate. For growth at 300 °C, the Fe/Co ratio drops to \( \sim 1:1 \) and remains constant over the time of deposition. At this temperature, the growth rate of Co on Co surface appears to slow down at larger thicknesses [based on one data point in Fig. 1(b)]; therefore, in Fig. 3(d), it is possible that the growth rate for Fe also slows down such that the Fe/Co ratio remains constant.

Our previous study of the CVD of \( \text{Fe}_x \text{Co}_{(1-x)} \) from \( \text{Fe} (\text{CO})_5 \) and \( \text{Co}_2 (\text{CO})_8 \) also showed that the composition of the deposit was a highly nonlinear function of the ratio of the partial pressures of the two precursors. Specifically, at a growth temperature of 210 °C, the amount of Fe in the film was 70% for Fe:Co precursor pressure ratios just above 2:1 but decreased abruptly to only 36% at a Fe:Co precursor pressure ratio just under 2:1. Furthermore, the microstructure changed from columnar at Fe:Co ratios over 2:1 to smooth and dense at Fe:Co ratios below 2:1. We can now add that identical behavior is seen at 200 °C (Fig. 4).

2. \( \text{Fe}_x \text{Co}_{(1-x)} \) growth in the presence of ammonia

A key result of the present work is that the addition of \( \text{NH}_3 \) during alloy growth eliminates all of the effects due to surface poisoning and considerably widens the process window for \( \text{Fe}_x \text{Co}_{(1-x)} \) growth, just as it eliminates poisoning during the growth of pure Fe films. Specifically, under growth conditions identical to those described above [0.10 mTorr \( \text{Fe} (\text{CO})_5 \) and 0.05 mTorr \( \text{Co}_2 (\text{CO})_8 \) for 10 min] except that 4 mTorr of \( \text{NH}_3 \) is added to the flux, the Fe/Co ratio of 3:1 is constant as a function of depth, and the film morphology is columnar. These attributes are independent of substrate temperatures over a wide range, from 200 to 300 °C (Fig. 5). The film composition and morphology are similar to those seen only at the lowest temperatures (175 °C) in the absence of \( \text{NH}_3 \) coflow.

![Fig. 5. SEM cross-sectional images and Auger sputter depth profiles of \( \text{Fe}_x \text{Co}_{(1-x)} \) alloy films grown from 0.10 mTorr \( \text{Fe} (\text{CO})_5 \) and 0.05 mTorr \( \text{Co}_2 (\text{CO})_8 \) for 10 min with a coflow of 4 mTorr \( \text{NH}_3 \) at (a) 200, (b) 250, (c) 300 °C. The film at 200 °C has a higher oxygen content due to air oxidation of the intercolumn void space, which is enhanced for low temperature growth.](image)

![Fig. 6. SEM cross-sectional image and Auger sputter depth profile of \( \text{Fe}_x \text{Co}_{(1-x)} \) alloy grown at 200 °C for 10 min from 0.05 mTorr \( \text{Co}_2 (\text{CO})_8 \) and 0.05 mTorr \( \text{Fe} (\text{CO})_5 \) with a coflow of 4 mTorr \( \text{NH}_3 \). The oxygen content, which is very high at the surface and decreases with depth, corresponds to oxidation of the column boundaries during postgrowth air exposure; the Fe/Co ratio is constant. In an identical sample capped \textit{in situ} with HfB\(_2\) diffusion barrier, the bulk oxygen content is constant at about 1 at. %](image)
Adding NH₃ to the gas stream again eliminated the poisoning effect seen for feeds with Fe:Co pressure ratios below 2:1, as evidenced by the faceted surface morphology and the constant composition as a function of depth seen for a film grown from a 1:1 Fe:Co precursor partial pressure ratio (Fig. 6). As discussed in our earlier work on growth of Fe from Fe(CO)₅, we believe that NH₃ inhibits the dissociative chemisorption of CO and promotes its desorption as intact molecules; hence, surface poisoning by adsorbed C is avoided.

3. Magnetic properties of FeₓCo₁₋ₓ films

Growth from a mixture of Fe(CO)₅ and Co₂(CO)₈ in the presence of a coflow of NH₃ affords a stable film composition within a wide temperature window, and the stoichiometry can be finely tuned by adjusting the precursor pressure ratio. A series of FeₓCo₁₋ₓ films with x = 0.70, 0.60, 0.55, and 0.45 (all ±0.02) were grown at 300 °C, then capped with HfB₂. Auger analyses (not shown) indicate that the oxygen content is 1–2 at. % for all the films and that the nitrogen content is below the detection limit of 1 at. %. The saturation magnetizations of these films are all >2 T. A film with composition Fe₀.₆₀Co₀.₄₀ exhibits the highest Bₛ of 2.33 T, which is, within experimental error, the same as the best FeₓCo₁₋ₓ films previously deposited by CVD.

IV. CONCLUSIONS

In the CVD of FeₓCo₁₋ₓ alloy thin film grown from the precursors Fe(CO)₅ and Co₂(CO)₈, we propose that dissociative chemisorption of carbon monoxide leads to a progressive buildup of surface carbon that poisons the growth surface and greatly affects the morphology and film stoichiometry. The poisoning effect is especially pronounced at elevated temperature or when using a large fraction of Co₂(CO)₈ in the gas mixture.

The results above show that adding a coflow of NH₃ during growth eliminates the surface poisoning effect, without introducing appreciable amounts of N into the deposit. NH₃ inhibits the dissociative chemisorption of CO and promotes its desorption as intact molecules, thus reducing the surface carbon atoms that are the cause of the surface poisoning effect. The ammonia restores the unpoisoned growth rate and morphology, makes the film stoichiometry depend linearly on the precursor flux ratio, and greatly expands the temperature window for the deposition of films with near ideal soft magnetic properties.

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